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(54) Title: PROCESS FOR DYEING KERATIN-CONTAINING FIBRES

(57) Abstract

Keratin-containing fibres, in particular human hair, are dyed using dyes of formulae (1) to (6) indicated in claim 1. These dyes make it possible to dye by the trichromatic principle even in dark shades.

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Process for dyeing keratin-containing fibres

The present invention relates to a process for dyeing keratin-containing fibres, in particular human hair, with cationic dyes.

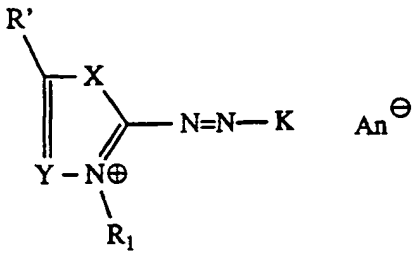
By far the largest proportion of all hair dyeings are carried out, even today, using so-called "oxidation colours", which involves applying small, colourless precursor molecules to the hair and reacting them by an oxidation process to form larger, coloured molecules. Although this produces the most durable ("permanent") colourings, increasing reservations are being voiced about possible toxicological risks posed not only by the substances used as starting materials but also by the oxidation intermediate and end products, whose precise composition is virtually uncontrollable. Further disadvantages are the relatively complicated use and in particular also the hair damage due to the aggressive chemicals used.

The other, so-called "semipermanent" and "temporary" colourings involve the use of ready-prepared dyes, primarily uncharged disperse dyes and relatively sparingly water-soluble acid dyes. Cationic dyes, by contrast, play only a very minor part. As the terms "semipermanent" and "temporary" indicate, these colourings only have a medium to poor fastness level. Especially the cationic dyes have a reputation for poor hydrolysis and light resistance and for uneven colouring of the hair, for example between root and tip (see: John F. Corbett: The Chemistry of Hair-care Products, JSDC August 1976, p. 290). In addition, the known cationic dyes have an insufficient build-up; i.e., even if increased amounts are used, it is impossible to exceed a certain, relatively low, colour strength. For instance, it is not possible to achieve a deep black coloration with the most important cationic hair dyes Basic Yellow 57, Basic Red 76, Basic Blue 99, Basic Brown 16 and Basic Brown 17 which are used in practice. For the same reason it is difficult to tint relatively dark natural hair with these dyes.

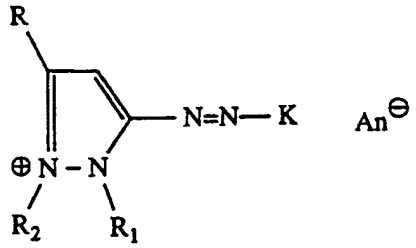
It has now been found that surprisingly cationic dyes of the below-indicated formulae have none of these disadvantages. They can be used to achieve in a very simple way and under gentle conditions very deep dyeings having excellent light, shampooing and crock

fastness properties. Owing to their extremely clean shades, they also extend the range of possible mixed shades considerably, especially in the direction of the increasingly important brilliant fashion colours.

The present invention accordingly provides a process for dyeing keratin-containing fibres, which comprises treating the fibres with a dye of the formula



(1),



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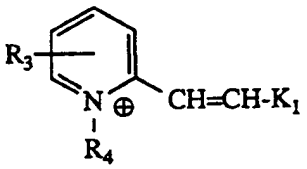

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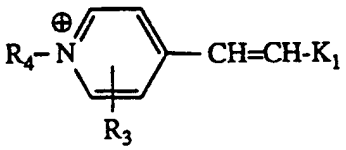

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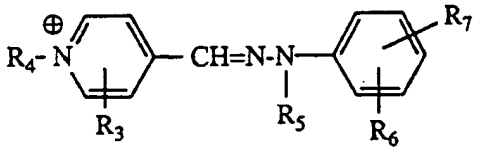

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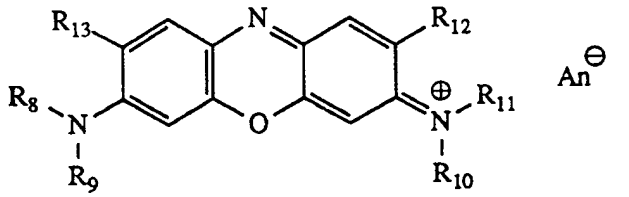


(6)

where

X is -O-, -S- or $-\underset{\underset{R_2}{|}}{N}-$,

Y is -CH=, $-\underset{\underset{R_2}{|}}{C}=$ or -N=,

R is hydrogen, C_1-C_4alkyl, Cl or nitro,

R' is hydrogen, C_1-C_4alkyl, Cl, nitro, amino, C_1-C_4monoalkylamino or di-C_1-C_4alkylamino,

R_1 and R_2 are each independently of the other unsubstituted or OH-, C_1-C_4alkoxy-, halogen-, CN-, amino-, C_1-C_4monoalkylamino- or di-C_1-C_4alkylamino-substituted C_1-C_4alkyl,

R_3 is hydrogen, C_1-C_4alkyl or CN,

R_4 is unsubstituted or OH- or CN-substituted C_1-C_4alkyl,

R_5 is hydrogen or C_1-C_4alkyl,

R_6 and R_7 are each independently of the other hydrogen, C_1-C_4alkyl or C_1-C_4alkoxy, or

R_5 and R_6 are together with the nitrogen and carbon atoms joining them together a 5- or 6-membered ring,

R_8, R_9, R_{10} and R_{11} are each independently of the others hydrogen or C_1-C_4alkyl, with the proviso that at least one of these 4 substituents is C_1-C_4alkyl and that not all four substituents are ethyl,

R_{12} and R_{13} are each independently of the other hydrogen, C_1-C_4alkyl or C_1-C_4alkoxy,

K is the radical of a coupling component of the aniline or phenol series or the radical of a heterocyclic coupling component,

K_1 is the radical of an aromatic or heterocyclic amine, and

$An^{\ominus}$ is a colourless anion, with the proviso that, in the dyes of the formula (1), K is not a radical of N,N-dimethylaniline when X is $-\underset{\underset{CH_3}{|}}{N}-$, Y is -N= and R and R_1 are each

methyl.

For the purposes of the present invention, alkyl radicals are generally straight-chain or branched C_1-C_4alkyl groups. Suitable are for example methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl or tert-butyl.

Suitable alkoxy radicals are those having 1 to 4 carbon atoms, e.g. methoxy, ethoxy, propoxy, isopropoxy, n-butoxy, isobutoxy or tert-butoxy.

Halogen is to be understood as meaning fluorine, bromine, iodine or in particular chlorine.

If R_5 and R_6 are combined with the nitrogen atom and two carbon atoms joining them together into a 5- or 6-membered ring, this ring may contain a further heteroatom, for example oxygen or sulfur. Moreover, the ring may be substituted, for example by hydroxyl, alkoxy, alkyl, halogen, CN or phenyl, or carry a further fused-on benzene ring. Preferred rings formed by R_5, R_6, the linked carbon atoms and the nitrogen atom are pyrroline, dihydrooxazine and di- or tetrahydropyridine rings carrying 0 to 4 methyl groups.

Suitable anions $An^{\ominus}$ include organic as well as inorganic anions, for example chloride, bromide, sulfate, hydrogensulfate, methosulfate, phosphate, borotetrafluoride, carbonate, bicarbonate, oxalate, formate, acetate, propionate, lactate or complex anions, such as the anion of zinc chloride double salts.

The anion is generally given by the method of preparation. Preferred anions are chloride, sulfate, hydrogensulfate, methosulfate, phosphate, formate, acetate or lactate.

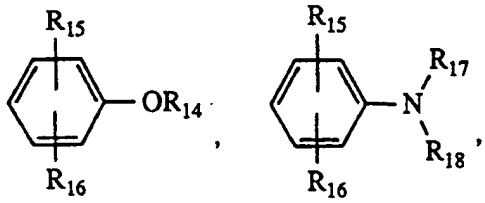
To dye by the process of the invention it is preferable to use a dye of the formula (1) where R' is hydrogen, C_1-C_2alkyl, amino, C_1-C_2monoalkylamino or di-C_1-C_2alkylamino or a dye of the formula (1) where R_1 is unsubstituted C_1-C_4alkyl.

It is likewise preferable to use dyes of the formula (2) where R is hydrogen or C_1-C_4alkyl or a dye of the formula (2) where R_1 is unsubstituted C_1-C_4alkyl.

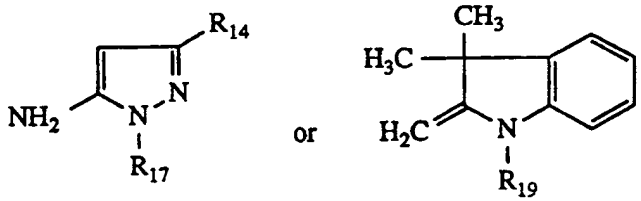
Of the dyes of the formula (1), preference is given to those where X is $-\underset{\displaystyle R_2}{\overset{\displaystyle |}{N}}-$ and

especially those where X is $-\underset{\underset{R_2}{|}}{N}-$ and Y is -CH=.

In the dyes of the formula (1), K is in particular the radical of a coupling component of the formula



(7) (8) (9)



(10) (11)

where

R_{14} is hydrogen or unsubstituted or OH-, C_1-C_4alkoxy-, halogen-, CN-, amino-, C_1-C_4monoalkylamino- or di-C_1-C_4alkylamino-substituted C_1-C_4alkyl,

R_{15} and R_{16} are each independently of the other hydrogen, C_1-C_4alkyl, C_1-C_4alkoxy or halogen,

R_{17} and R_{18} are each independently of the other hydrogen, unsubstituted or OH-, C_1-C_4alkoxy-, halogen-, CN-, amino-, C_1-C_4monoalkylamino- or di-C_1-C_4alkylamino-substituted C_1-C_4alkyl, or

R_{17} and R_{18} are together with the nitrogen atom joining them together a 5- or 6-membered ring, or

R_{15} and R_{17} are together with the nitrogen and carbon atoms joining them together a 5- or 6-membered ring, or

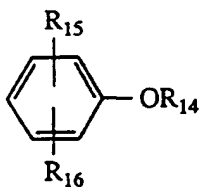
R_{16} and R_{18} are together with the nitrogen and carbon atoms joining them together a 5- or 6-membered ring, and

R_{19} is hydrogen or unsubstituted or OH-, C_1-C_4alkoxy-, halogen-, CN-, amino-, C_1-C_4monoalkylamino- or di-C_1-C_4alkylamino-substituted C_1-C_4alkyl.

If R_{17} and R_{18} are to combine with the nitrogen atom joining them together into a 5- or 6-membered ring, this ring is in particular a pyrrolidine, piperidine, morpholine or piperazine ring. These rings can be further substituted, for example by C_1-C_4alkyl or C_1-C_4alkoxy. Preference, however, is given to the unsubstituted rings.

If R_{15} and R_{17} or R_{16} and R_{18} are combined with the nitrogen atom and the two carbon atoms joining them together into a 5- or 6-membered ring, this ring may contain a further heteroatom, for example oxygen or sulfur. Moreover, the ring may be substituted, for example by hydroxyl, alkoxy, alkyl, halogen or CN, or carry a further fused-on benzene ring. Preferred rings formed by R_{15} and R_{17} or R_{16} and R_{18} and the carbon atoms joining them together and the nitrogen atom are pyrroline, dihydrooxazine and di- or tetrahydropyridine rings carrying 0 to 4 methyl groups.

In particular K is the radical of a coupling component of the formula



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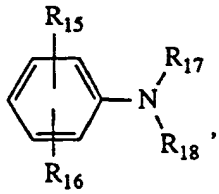


(7) (8)

where

R_{14} is hydrogen or unsubstituted C_1-C_4alkyl,

R_{15} and R_{16} are each independently of the other hydrogen, C_1-C_4alkyl, C_1-C_4alkoxy or halogen,

R_{17} and R_{18} are each independently of the other hydrogen or unsubstituted C_1-C_4alkyl, or

R_{17} and R_{18} are together with the nitrogen atom joining them together a pyrrolidine, piperidine, morpholine or piperazine ring, or

R_{15} and R_{17} are together with the nitrogen and carbon atom joining them together a pyrrolidine, piperidine, morpholine or piperazine ring, or

R_{16} and R_{18} are together with the nitrogen and carbon atom joining them together a pyrrolidine, piperidine, morpholine or piperazine ring, and

R_{19} is hydrogen or unsubstituted C_1-C_4alkyl.

Of very particular interest for the process of the invention are dyes of the formula (1) or (2) where K is the radical of a coupling component of the formula (7) or (8) where

R_{14} is methyl or ethyl,

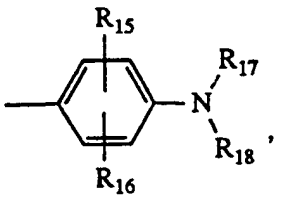
R_{15} and R_{16} are each independently of the other hydrogen, methyl, ethyl, methoxy, ethoxy or chlorine,

R_{17} and R_{18} are each independently of the other hydrogen, methyl or ethyl, and

R_{19} is hydrogen, methyl or ethyl.

Preference is also given to using a dye of the formula (3), (4) or (5) where R_3 is hydrogen or methyl or a dye of the formula (3), (4) or (5) where R_4 is unsubstituted or hydroxyl-substituted C_1-C_4alkyl, in particular methyl.

In the dyes of the formula (3) and (4), K_1 is in particular the radical of an amine of the formula



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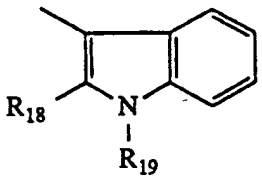

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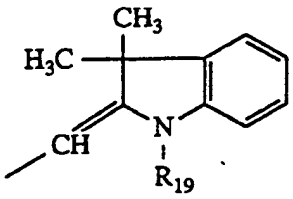
or



(14)

where

R_{15} and R_{16} are each independently of the other hydrogen, C_1-C_4alkyl, C_1-C_4alkoxy or halogen,

R_{17} and R_{18} are each independently of the other hydrogen, unsubstituted or OH-, C_1-C_4alkoxy-, halogen-, CN-, amino-, C_1-C_4monoalkylamino- or di-C_1-C_4alkylamino-substituted C_1-C_4alkyl, or

R_{17} and R_{18} are together with the nitrogen atom joining them together a 5- or 6-membered ring, or

R_{15} and R_{17} are together with the nitrogen and carbon atoms joining them together a 5- or 6-membered ring, or

R_{16} and R_{18} are together with the nitrogen and carbon atoms joining them together a 5- or 6-membered ring, and

R_{19} is hydrogen or unsubstituted or OH-, C_1-C_4alkoxy-, halogen-, CN-, amino-,

C_1-C_4monoalkylamino- or di-C_1-C_4alkylamino-substituted C_1-C_4alkyl,
and in particular the radical of an amine of the formula (12), (13) or (14), where
R_{15} and R_{16} are each independently of the other hydrogen, methyl, ethyl, methoxy, ethoxy or chlorine, or
R_{15} and R_{17} are together with the nitrogen and carbon atoms joining them together a pyrrolidine, piperidine, morpholine or piperazine ring,
R_{17} and R_{18} are each independently of the other hydrogen, methyl or ethyl, and
R_{19} is hydrogen, methyl or ethyl.

If the process of the invention is carried out using a dye of the formula (5), it is in particular a dye of the formula (5) where
R_5 is hydrogen or methyl and R_6 and R_7 are each independently of the other hydrogen, C_1-C_2alkyl or C_1-C_2alkoxy, or
R_5 and R_6 are together with the nitrogen and carbon atoms joining them together a pyrrolidine, piperidine, morpholine or piperazine ring.

Of the dyes of the formula (6), preference is given to using those where
R_8, R_9, R_{10} and R_{11} are each independently of the others hydrogen or C_1-C_2alkyl, with the proviso that at least one of these 4 substituents is C_1-C_2alkyl and that not all four substituents are ethyl, and
R_{12} and R_{13} are each independently of the other hydrogen, C_1-C_2alkyl or C_1-C_2alkoxy.

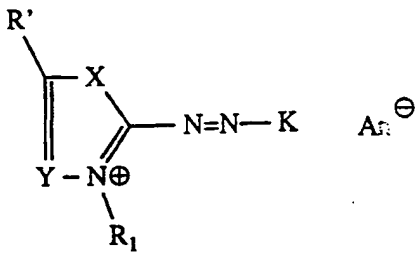
The dyes used according to the invention are known or can be prepared in a manner known per se.

The present invention furthermore provides a process for dyeing keratin-containing fibres, which comprises treating the fibres with a mixture of at least two cationic dyes having a delocalized positive charge and a cation weight below 300, preferably below 280.

Preference is given to using a mixture of at least three cationic dyes with a delocalized positive charge and a cation weight below 280 and in particular a mixture of a yellow, a red and a blue cationic dye with delocalized positive charge and a cation weight below 280.

A very particularly preferred embodiment of the novel process for dyeing keratin-containing fibres comprises treating the fibres with a mixture of at least two

cationic dyes of the formula



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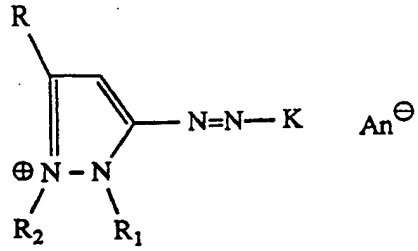

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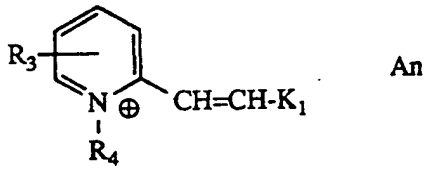

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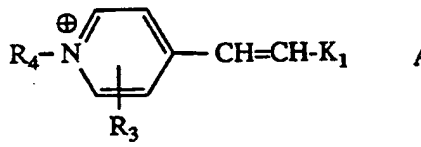

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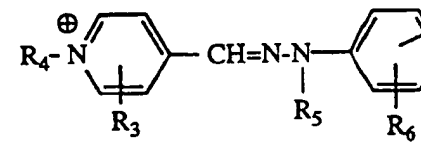

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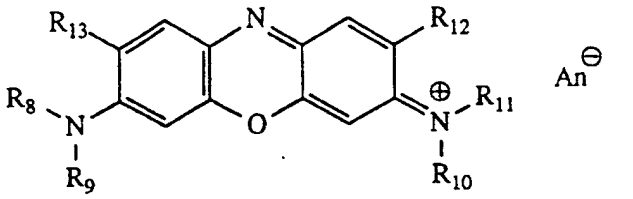


(6)

where

X is -O-, -S- or $-\overset{|}{\underset{R_2}{N}}-$,

Y is -CH=, $-\overset{|}{\underset{R_2}{C}}=$ or -N=,

R is hydrogen, C_1-C_4alkyl, Cl or nitro,

R' is hydrogen, C_1-C_4alkyl, Cl, nitro, amino, C_1-C_4monoalkylamino or di-C_1-C_4alkylamino,

R_1 and R_2 are each independently of the other unsubstituted or OH-, C_1-C_4alkoxy-, halogen-, CN-, amino-, C_1-C_4monoalkylamino- or di-C_1-C_4alkylamino-substituted C_1-C_4alkyl,

R_3 is hydrogen, C_1-C_4alkyl or CN,

R_4 is unsubstituted or OH- or CN-substituted C_1-C_4alkyl,

R_5 is hydrogen or C_1-C_4alkyl,

R_6 and R_7 are each independently of the other hydrogen, C_1-C_4alkyl or C_1-C_4alkoxy, or

R_5 and R_6 are together with the nitrogen and carbon atoms joining them together a 5- or 6-membered ring,

R_8, R_9, R_{10} and R_{11} are each independently of the others hydrogen or C_1-C_4alkyl,

R_{12} and R_{13} are each independently of the other hydrogen, C_1-C_4alkyl or C_1-C_4alkoxy,

K is the radical of a coupling component of the aniline series or the radical of a heterocyclic coupling component,

K_1 is the radical of an aromatic or heterocyclic amine, and

$An^{\ominus}$ is a colourless anion.

The process of the invention is suitable for dyeing furs and also animal and human hair, especially live human hair and domestic animals' hair. As a consequence of the high affinity and the good water solubility of the dyes used, it is possible to do the dyeing at room temperature from aqueous solutions without any assistants whatsoever.

However, it is also possible to use any assistants customary for cationic dyes used in the dyeing of hair, for example wetting agents, swelling agents, penetration aids or scents. In addition, the dyes can be incorporated into shampoos, creams, gels or pastes. Such cosmetic formulations for dyeing hair comprising at least one dye of the above-indicated formulae (1) to (6) and also assistants form a further part of the subject-matter of the present invention.

It has been found that the dyeing effect of the dyes used depends relatively little on the formulation of the dyes.

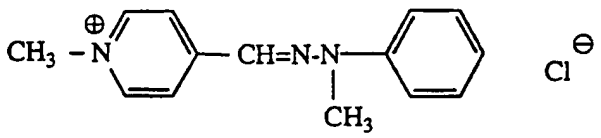
A particular advantage of the dyes used according to the invention for dyeing hair is that, owing to the good build-up of the dyes, the colourings can be prepared by the trichromatic principle; that is, it is possible by using a yellow, a red and a blue dye in suitable mixtures of these dyes to achieve virtually all shades. In addition, exact prediction of the shades obtained is possible, which is not the case with the so-called "oxidation dyes" owing to the varying composition of the end products.

Using colorimetric methods of measurement it is also possible to obtain on natural, unbleached hair predicted shades having regard to the hair's natural colour by determining its yellow, red and blue content and deducting it from the recipe of the desired shade. This is not feasible with the hair dyes previously used.

The colourings obtained are crock-, water-, wash- and light-fast and stable to permanent-deformation agents, for example thioglycolic acid.

The Examples which follow illustrate the invention. Parts and percentages are by weight. The temperatures are given in degrees Celsius.

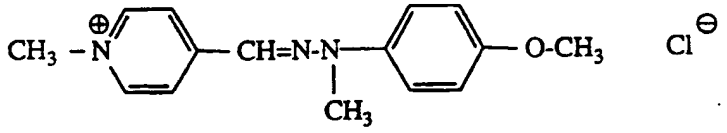
Example 1: A braid-sewn strand of blond, natural, untreated human hair is dyed at 25°C for 5 minutes in a conventional manner with a dye emulsion containing 0.1 % of the dye of the formula



3.5 % of Cetearyl Alcohol
1.0 % of Ceteareth 80
0.5 % of glyceryl mono-di-stearate
3.0 % of stearamide DEA
1.0 % of stearamphopropylsulfonate
0.5 % of polyquaternium-6 and
water to 100 %.

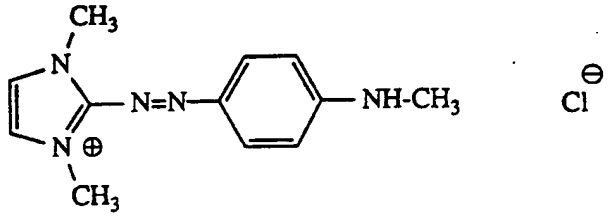
Then the hair is thoroughly rinsed with water and air-dried. The result is an intensive brilliant yellow colouring which is many times stronger than a colouring prepared with Basic Yellow 57 in the same way. The light, shampooing and friction fastness properties of the colouring according to the invention are excellent.

Example 2: Example 1 is repeated with the dye of the formula



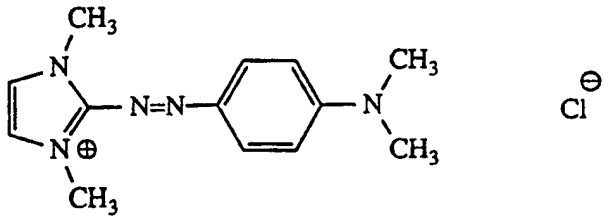
affording an intensively golden yellow colouring with likewise excellent fastness properties.

Example 3: A 1 % solution of the dye of the formula



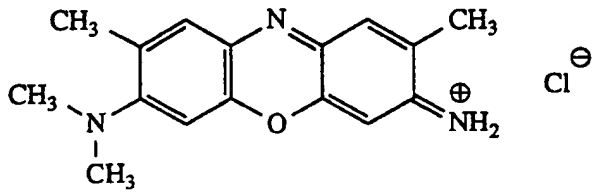
in a surfactant base containing 10 % of cocoamphoglycinate and 90 % of water is applied to Chinese, bleached yak hair at 25°C for 5 minutes, and then the hair is thoroughly rinsed and air-dried. The intensively scarlet red colouring obtained is many times stronger than a comparative dyeing with Basic Red 76 and also of distinctly better light fastness.

Example 4: A strand of medium brown, untreated human hair is dyed for 5 minutes at room temperature with a dye emulsion containing 0.1 % of the dye of the formula



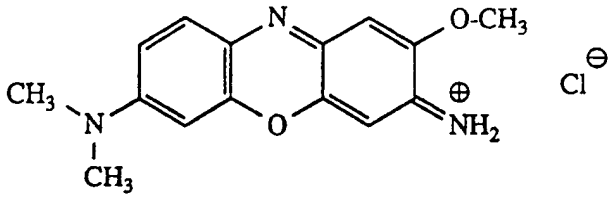
and otherwise having the same composition as the dye emulsion of Example 1. Then the strand of hair is thoroughly rinsed with water and air-dried. The result is a very attractive chestnut-brown shade of the kind which is frequently desired. This shade is impossible to achieve with Basic Red 76 on account of the insufficient build-up of this dye.

Example 5: A strand of bleached yak hair is dyed for 5 minutes at 25°C with a dye emulsion which contains 0.1 % of the dye of the formula



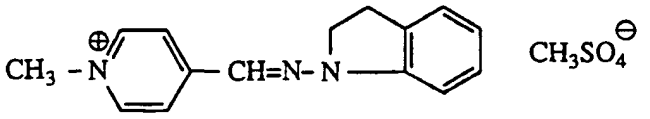
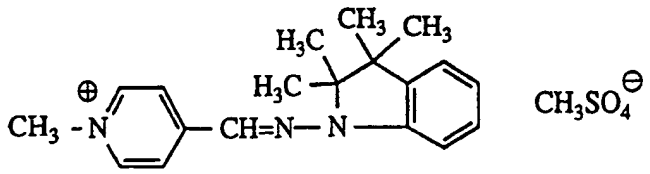
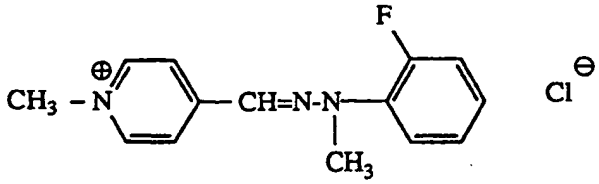
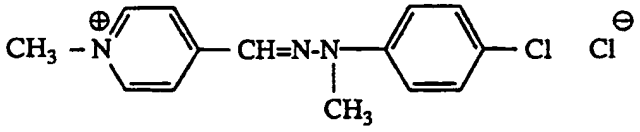
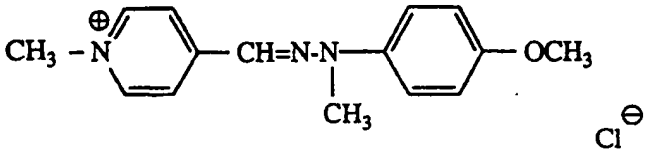
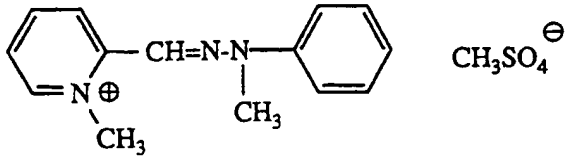
and otherwise has the same composition as the dye emulsion of Example 3. Then the strand of hair is thoroughly rinsed with water and air-dried. The blue colouring obtained is very significantly stronger and more brilliant than a dyeing with Basic Blue 99 prepared in the same way.

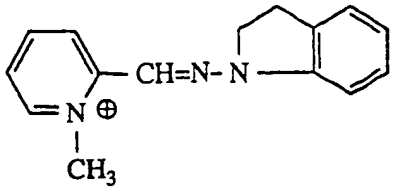
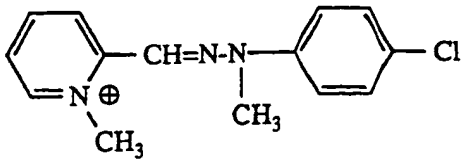
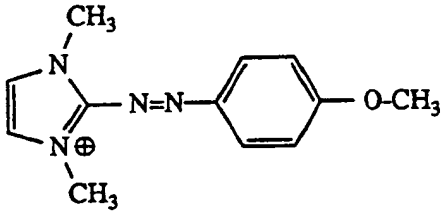
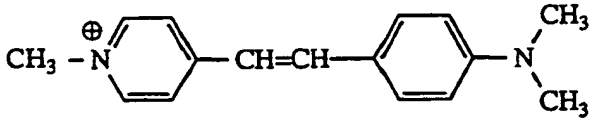
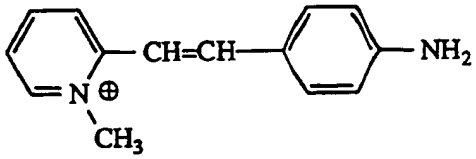
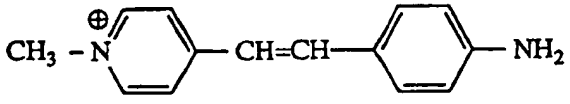
Example 6: Example 4 is repeated with the red dye replaced by the blue dye of the formula

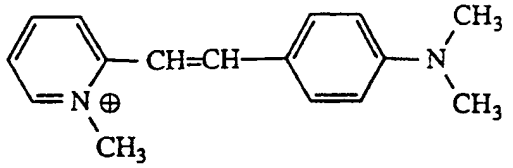


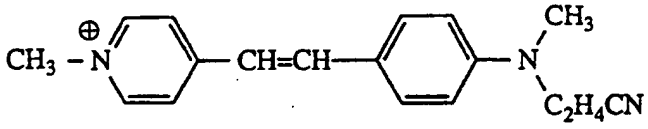
This shifts the original brown of the hair to a mattish brown hue which hides very well undesirable rust-red shades as frequently obtained following oxidation dyeings and lightenings. The scope for these tinting uses is much less with Basic Blue 99.

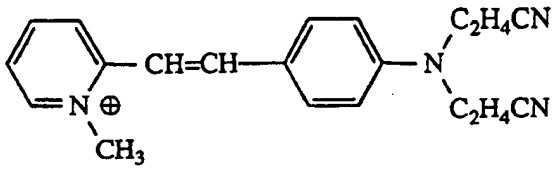
Examples 7-70: The method of Examples 1-3 is applied with the dyes listed below in the table, affording colourings on the hair in the specified hues.

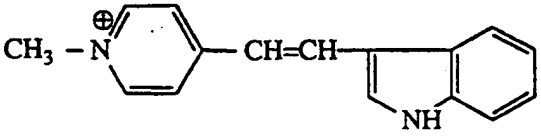
Example	Dye	Hue
7		yellow
8		yellow
9		yellow
10		yellow
11		yellow
12		yellow

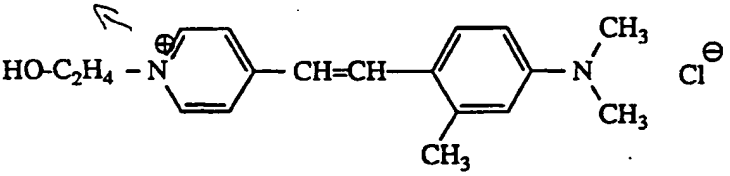
13		$CH_3SO_4^{\ominus}$	yellow
14		$CH_3SO_4^{\ominus}$	yellow
15		$Cl^{\ominus}$	yellow
16		$Cl^{\ominus}$	orange
17		$CH_3COO^{\ominus}$	greenish yellow
18		$CH_3COO^{\ominus}$	greenish yellow

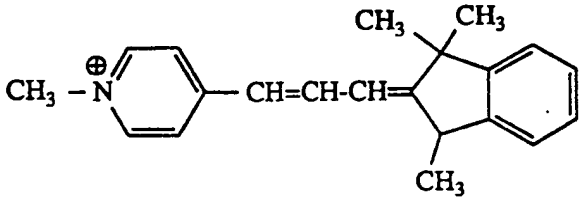
19  orange

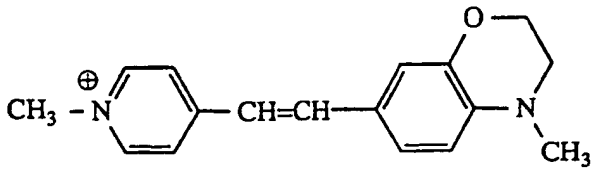
20  yellowish orange

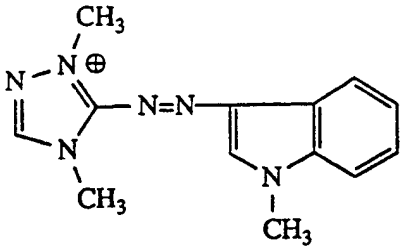
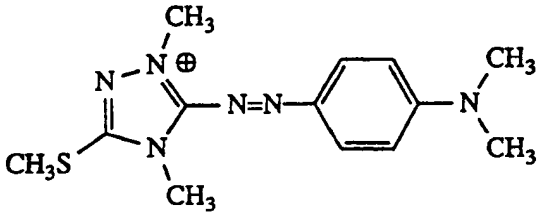
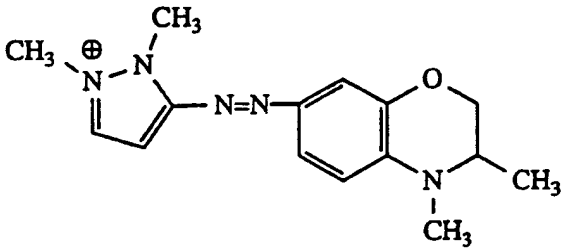
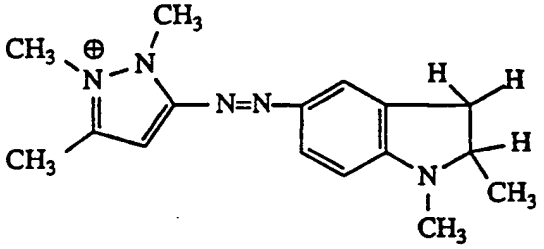
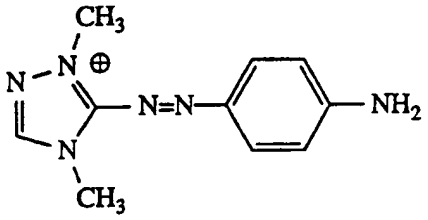
21  yellow

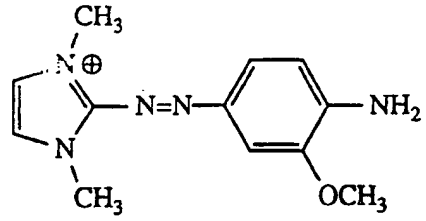
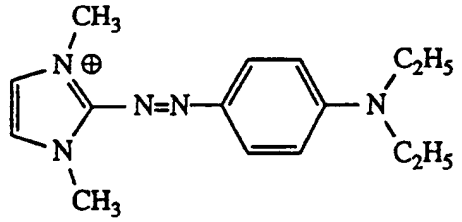
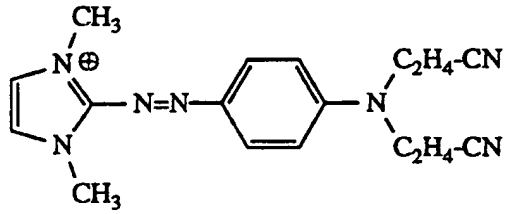
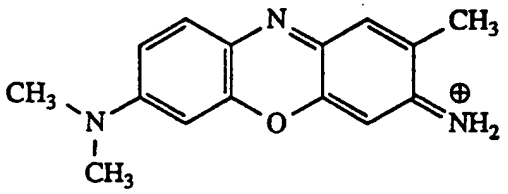
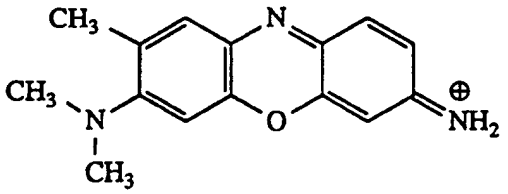
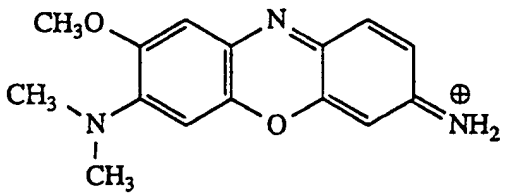
22  greenish yellow

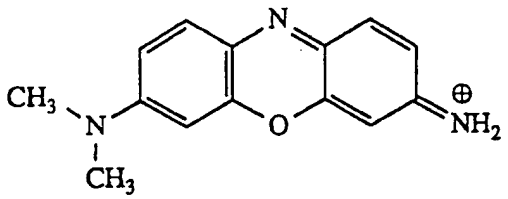
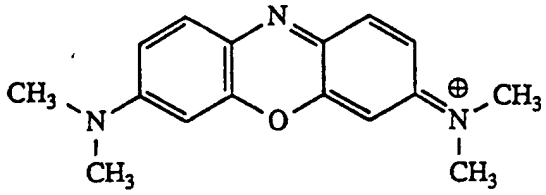
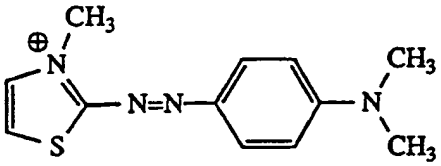
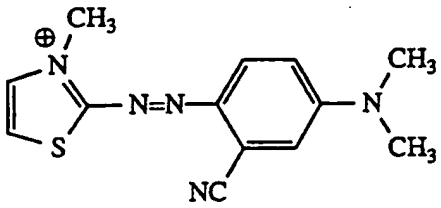
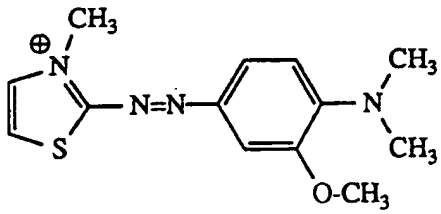
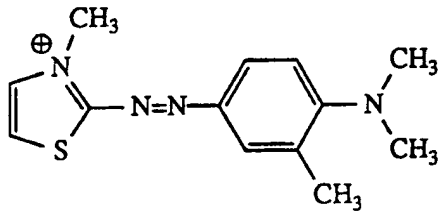
23  reddish orange

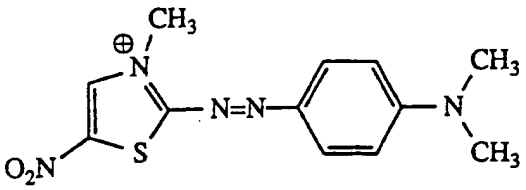
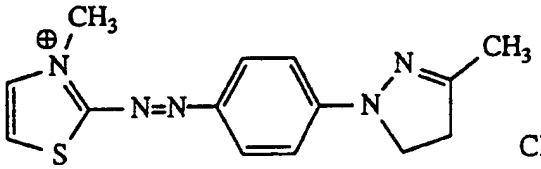
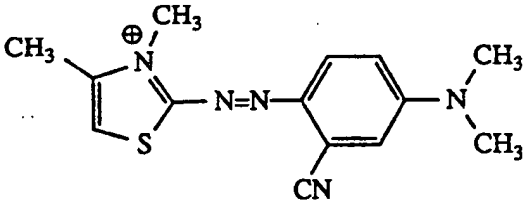
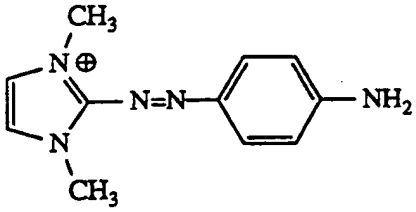
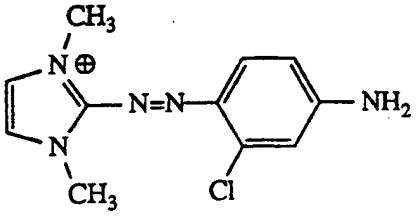
24  red

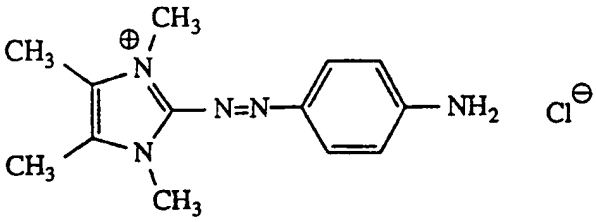
25  scarlet

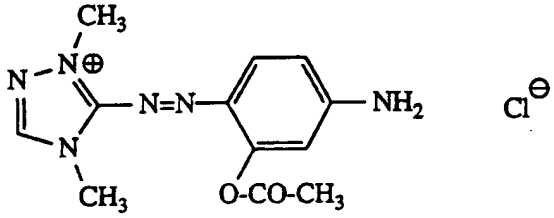
26		$Cl^{\ominus}$	golden yellow
27		$Cl^{\ominus}$	red
28		$Cl^{\ominus}$	red
29		$Cl^{\ominus}$	red
30		$Cl^{\ominus}$	reddish orange

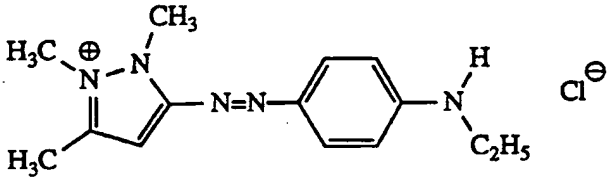
31		$Cl^{\ominus}$	red
32		$Cl^{\ominus}$	red
33		$Cl^{\ominus}$	red
34		$Cl^{\ominus}$	blue
35		$Cl^{\ominus}$	blue
36		$Cl^{\ominus}$	blue

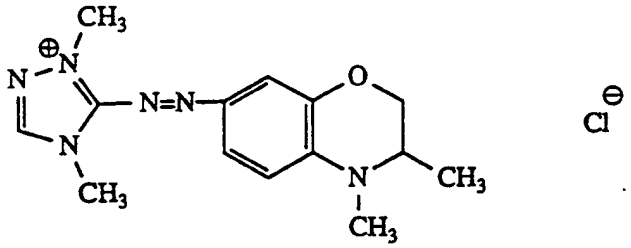
37		$Cl^{\ominus}$	blue
38		$Cl^{\ominus}$	blue
39		$Cl^{\ominus}$	blue
40		$Cl^{\ominus}$	blue
41		$Cl^{\ominus}$	blue
42		$Cl^{\ominus}$	blue

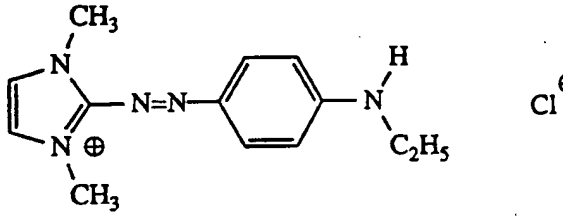
43		$Cl^{\ominus}$	blue
44		$CH_3SO_4^{\ominus}$	blue
45		$Cl^{\ominus}$	blue
46		$Cl^{\ominus}$	orange
47		$Cl^{\ominus}$	orange

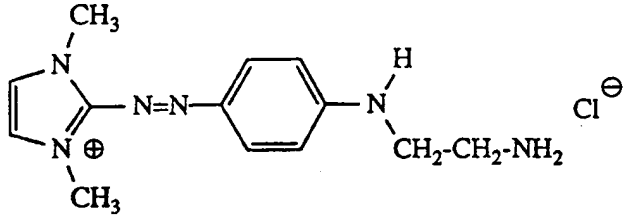
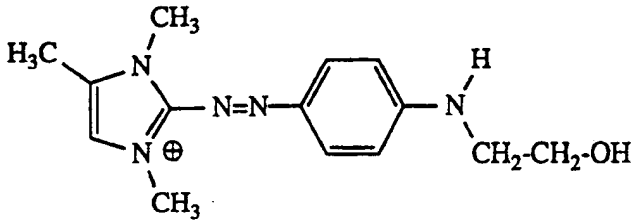
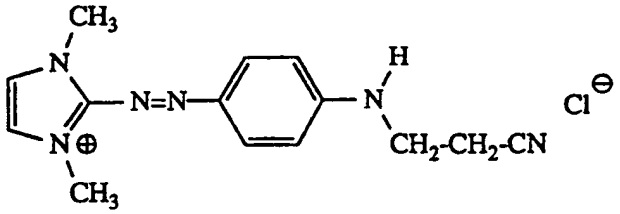
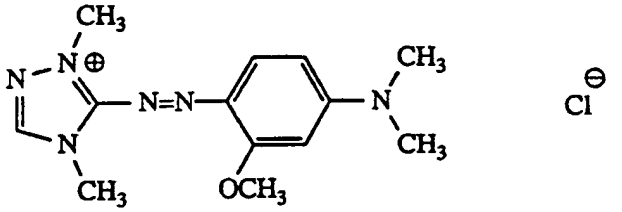
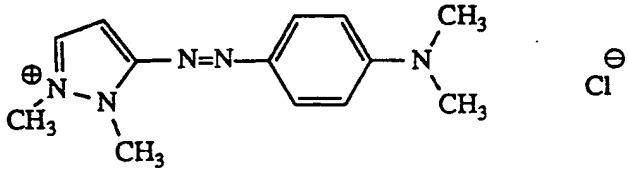
48  orange

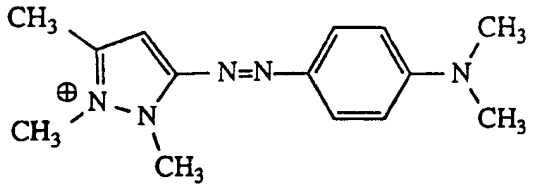
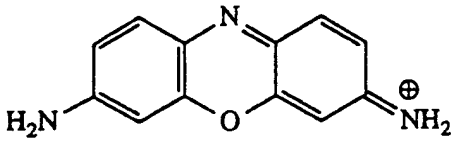
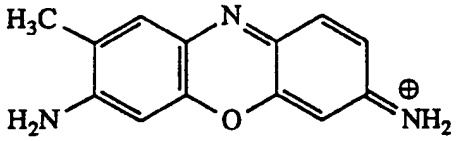
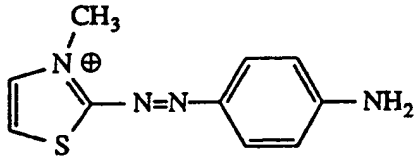
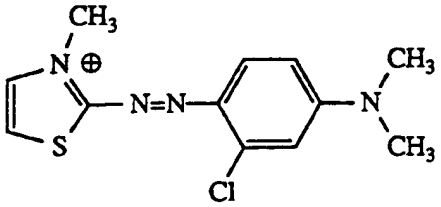
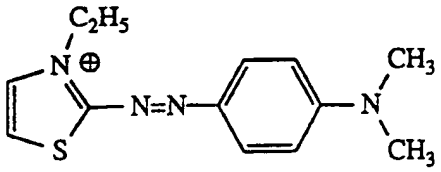
49  reddish orange

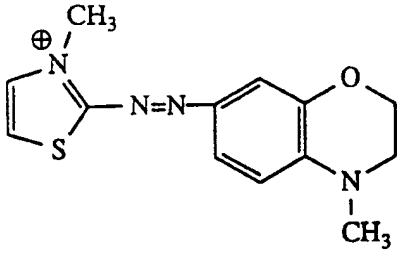
50  orange

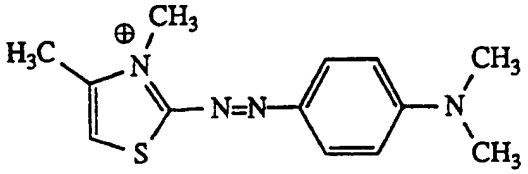
51  ruby

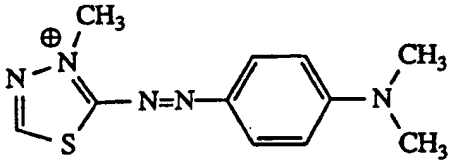
52  scarlet

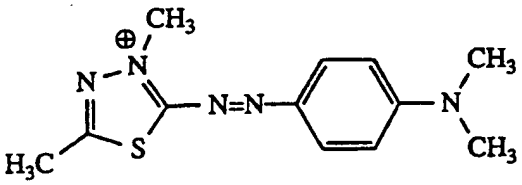
53		$Cl^{\ominus}$	scarlet
54		$Cl^{\ominus}$	scarlet
55		$Cl^{\ominus}$	scarlet
56		$Cl^{\ominus}$	scarlet
57		$Cl^{\ominus}$	scarlet

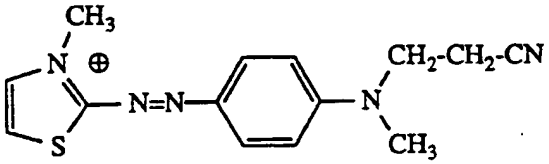
58		$Cl^{\ominus}$	scarlet
59		$Cl^{\ominus}$	violet
60		$Cl^{\ominus}$	violet
61		$Cl^{\ominus}$	violet
62		$CH_3SO_4^{\ominus}$	blue
63		$CH_3SO_4^{\ominus}$	blue

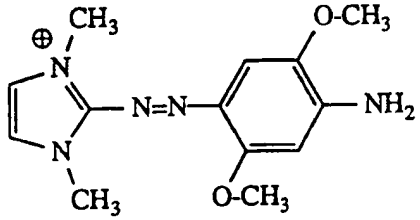
64  $Cl^{\ominus}$ blue

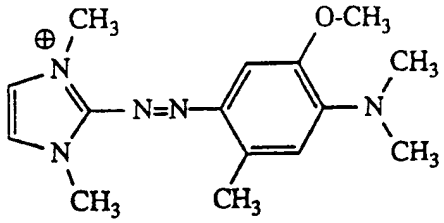
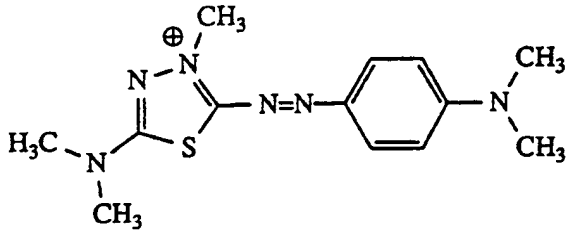
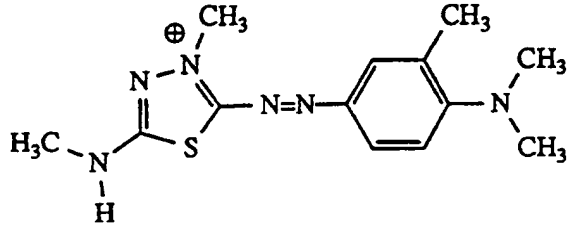
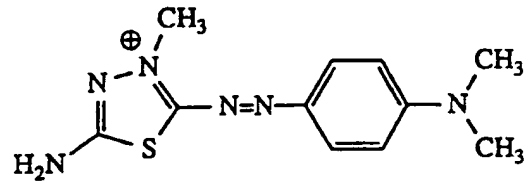
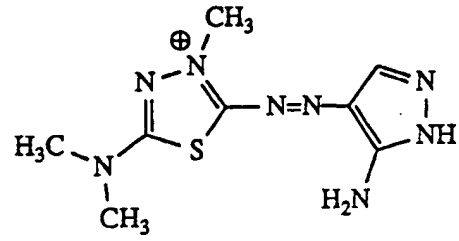
65  $CH_3SO_4^{\ominus}$ bluish violet

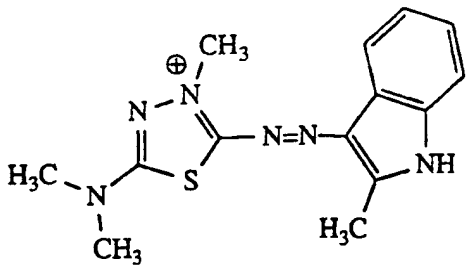
66  $CH_3SO_4^{\ominus}$ bluish violet

67  $CH_3SO_4^{\ominus}$ blue

68  $Cl^{\ominus}$ violet

69  $Cl^{\ominus}$ violet

70		$Cl^{\ominus}$	violet
71		$CH_3SO_4^{\ominus}$	blue
72		$CH_3SO_4^{\ominus}$	blue
73		$CH_3SO_4^{\ominus}$	blue
74		$CH_3SO_4^{\ominus}$	blue

75  $CH_3SO_4^{\ominus}$ red

Example 76: A braided strand of blond, natural, untreated human hair is treated at 25°C for 5 minutes with a dye emulsion which has the same composition as the emulsion in Example 1 but contains as dyes 0.11 % of the dye of Example 4 and 0.10 % of the dye of Example 5. After the strand of hair has been thoroughly rinsed with water and dried, it has a deep violet colour with very good fastness properties.

Example 77: Example 76 is repeated with the dyes replaced by 0.08 % of the dye of Example 1 and 0.06 % of the dye of Example 5, affording a very brilliant green colouring on the hair.

Example 78: 0.02 % of the dye of Example 1 and 0.08 % of the dye of Example 5 are dissolved in a surfactant base comprising a 10 % aqueous solution of cocoamphoglycinate and this solution is used to dye a strand of bleached yak hair at room temperature for 5 minutes. A bright, brilliant turquoise shade is obtained on the hair.

Example 79: Blond, untreated human hair is treated for 20 minutes at room temperature with a dye emulsion which has the same composition as the emulsion in Example 1 but contains as dyes 0.2 % of the dye of Example 1, 0.1 % of the dye of Example 4 and 0.17 % of the dye of Example 6. Thorough rinsing and drying of the hair leaves a deep black colouring having good fastness properties.

Example 80: Example 79 is repeated with the dyes replaced by a dye mixture containing

0.138 % of the dye of Example 2,
0.082 % of the dye of Example 4 and
0.026 % of the dye of Example 6,

affording a chestnut brown colouring.

Example 81: Olive-coloured hair is obtained on repeating Example 79 with the following

dye mixture:

0.13 % of the dye of Example 2,
0.006 % of the dye of Example 4 and
0.032 % of the dye of Example 6.

Example 82: Example 81 is repeated with a dye mixture containing

0.01 % of the dye of Example 2,
0.11 % of the dye of Example 4 and
0.21 % of the dye of Example 6,

affording a dark navy colouring on the hair.

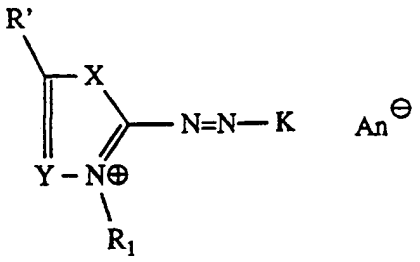
Example 83: A surfactant base comprising a 10 % aqueous solution of cocoamphoglycinate is used to dissolve

0.036 % of the dye of Example 1,
0.034 % of the dye of Example 2 and
0.06 % of the dye of Example 3

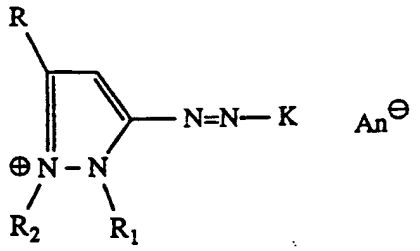
and this solution is used to treat a strand of bleached yak hair for 10 minutes at 25°C. Rinsing and drying leaves a luminously orange dyeing having excellent light, shampooing and friction fastness properties.

WHAT IS CLAIMED IS:

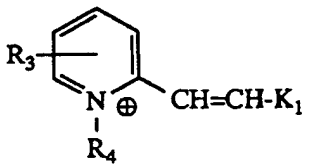
1. A process for dyeing keratin-containing fibres, which comprises treating the fibres with a dye of the formula



(1),



(2),



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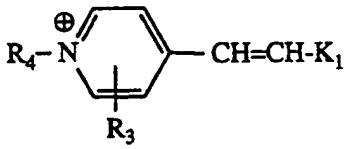

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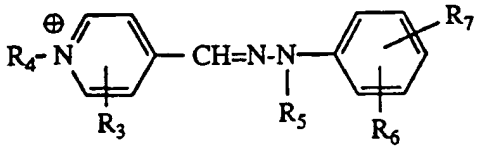
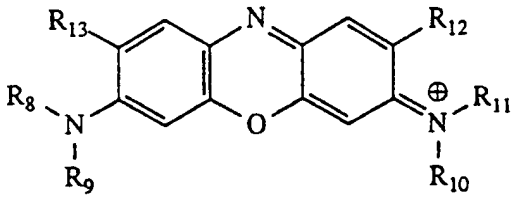


(5)

or



(6)

where

X is -O-, -S- or $-\underset{\underset{R_2}{|}}{N}-$,

Y is -CH=, $-\underset{\underset{R_2}{|}}{C}=$ or -N=,

R is hydrogen, C_1-C_4alkyl, Cl or nitro,

R' is hydrogen, C_1-C_4alkyl, Cl, nitro, amino, C_1-C_4monoalkylamino or di-C_1-C_4alkylamino,

R_1 and R_2 are each independently of the other unsubstituted or OH-, C_1-C_4alkoxy-, halogen-, CN-, amino-, C_1-C_4monoalkylamino- or di-C_1-C_4alkylamino-substituted C_1-C_4alkyl,

R_3 is hydrogen, C_1-C_4alkyl or CN,

R_4 is unsubstituted or OH- or CN-substituted C_1-C_4alkyl,

R_5 is hydrogen or C_1-C_4alkyl,

R_6 and R_7 are each independently of the other hydrogen, C_1-C_4alkyl or C_1-C_4alkoxy, or

R_5 and R_6 are together with the nitrogen and carbon atoms joining them together a 5- or 6-membered ring,

R_8, R_9, R_{10} and R_{11} are each independently of the others hydrogen or C_1-C_4alkyl, with the proviso that at least one of these 4 substituents is C_1-C_4alkyl and that not all four substituents are ethyl,

R_{12} and R_{13} are each independently of the other hydrogen, C_1-C_4alkyl or C_1-C_4alkoxy,

K is the radical of a coupling component of the aniline or phenol series or the radical of a heterocyclic coupling component,

K_1 is the radical of an aromatic or heterocyclic amine, and

$An^{\ominus}$ is a colourless anion, with the proviso that, in the dyes of the formula (1), K is not a radical of N,N-dimethylaniline when X is $-\underset{\underset{CH_3}{|}}{N}-$, Y is -N= and R and R_1 are each methyl.

2. A process according to claim 1, wherein the dye used has the formula (1) where R is hydrogen or C_1-C_4alkyl.

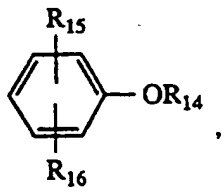
3. A process according to either of claims 1 and 2, wherein the dye used has the formula (1) or (2) where R_1 is unsubstituted C_1-C_4alkyl.

4. A process according to any one of claims 1 to 3, wherein the dye used has the formula (1) where R_1 is unsubstituted C_1-C_4alkyl.

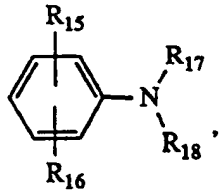
5. A process according to any one of claims 1 to 4, wherein the dye used has the formula (1) where X is $-\overset{R_2}{\underset{|}{N}}-$.

6. A process according to any one of claims 1 to 5, wherein the dye used has the formula (1) where X is $-\overset{R_2}{\underset{|}{N}}-$ and Y is -CH=.

7. A process according to any one of claims 1 to 6, wherein the dye used has the formula (1) or (2) where K is the radical of a coupling component of the formula



(7)



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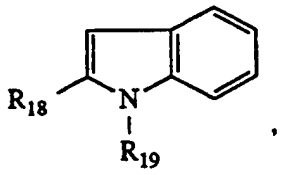
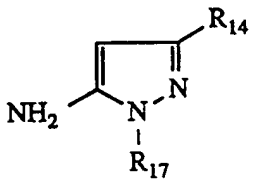
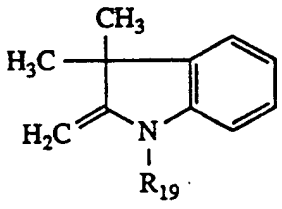


(9)



or



(10) (11)

where

R_{14} is hydrogen or unsubstituted or OH-, C_1-C_4alkoxy-, halogen-, CN-, amino-,

C_1-C_4monoalkylamino- or di-C_1-C_4alkylamino-substituted C_1-C_4alkyl,

R_{15} and R_{16} are each independently of the other hydrogen, C_1-C_4alkyl, C_1-C_4alkoxy or halogen,

R_{17} and R_{18} are each independently of the other hydrogen, unsubstituted or OH-, C_1-C_4alkoxy-, halogen-, CN-, amino-, C_1-C_4monoalkylamino- or di-C_1-C_4alkylamino-substituted C_1-C_4alkyl, or

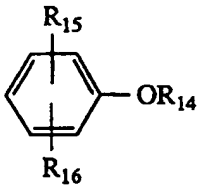
R_{17} and R_{18} are together with the nitrogen atom joining them together a 5- or 6-membered ring, or

R_{15} and R_{17} are together with the nitrogen and carbon atoms joining them together a 5- or 6-membered ring, or

R_{16} and R_{18} are together with the nitrogen and carbon atoms joining them together a 5- or 6-membered ring, and

R_{19} is hydrogen or unsubstituted or OH-, C_1-C_4alkoxy-, halogen-, CN-, amino-, C_1-C_4monoalkylamino- or di-C_1-C_4alkylamino-substituted C_1-C_4alkyl.

8. A process according to claim 7, wherein the dye used has the formula (1) where K is the radical of a coupling component of the formula



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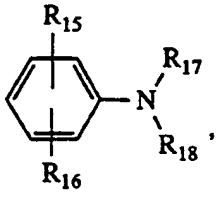


(7) (8)

where

R_{14} is hydrogen or unsubstituted C_1-C_4alkyl,

R_{15} and R_{16} are each independently of the other hydrogen, C_1-C_4alkyl, C_1-C_4alkoxy or halogen,

R_{17} and R_{18} are each independently of the other hydrogen or unsubstituted C_1-C_4alkyl, or

R_{17} and R_{18} are together with the nitrogen atom joining them together a pyrrolidine, piperidine, morpholine or piperazine ring, or

R_{15} and R_{17} are together with the nitrogen and carbon atom joining them together a pyrrolidine, piperidine, morpholine or piperazine ring, or

R_{16} and R_{18} are together with the nitrogen and carbon atom joining them together a pyrrolidine, piperidine, morpholine or piperazine ring, and

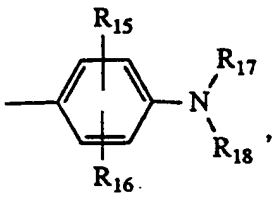
R_{19} is hydrogen or unsubstituted C_1-C_4alkyl.

9. A process according to claim 8, wherein the dye used has the formula (1) or (2) where
K is the radical of a coupling component of the formula (7) or (8) where
R_{14} is methyl or ethyl,
R_{15} and R_{16} are each independently of the other hydrogen, methyl, ethyl, methoxy, ethoxy or chlorine,
R_{17} and R_{18} are each independently of the other hydrogen, methyl or ethyl, and
R_{19} is hydrogen, methyl or ethyl.

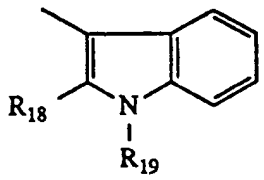
10. A process according to claim 1, wherein the dye used has the formula (3), (4) or (5) where R_3 is hydrogen or methyl.

11. A process according to claim 1, wherein the dye used has the formula (3), (4) or (5) where R_4 is unsubstituted or hydroxyl-substituted C_1-C_4alkyl, in particular methyl.

12. A process according to claim 1, wherein the dye used has the formula (3) or (4) where K_1 is the radical of an amine of the formula

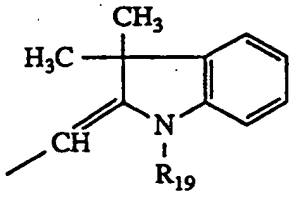


(12)



(13)

or



(14)

where
R_{15} and R_{16} are each independently of the other hydrogen, C_1-C_4alkyl, C_1-C_4alkoxy or halogen,
R_{17} and R_{18} are each independently of the other hydrogen, unsubstituted or OH-, C_1-C_4alkoxy-, halogen-, CN-, amino-, C_1-C_4monoalkylamino- or di-C_1-C_4alkylamino-substituted C_1-C_4alkyl, or
R_{17} and R_{18} are together with the nitrogen atom joining them together a 5- or 6-membered ring, or
R_{15} and R_{17} are together with the nitrogen and carbon atoms joining them together a 5- or

6-membered ring, or

R_{16} and R_{18} are together with the nitrogen and carbon atoms joining them together a 5- or 6-membered ring, and

R_{19} is hydrogen or unsubstituted or OH-, C_1-C_4alkoxy-, halogen-, CN-, amino-, C_1-C_4monoalkylamino- or di-C_1-C_4alkylamino-substituted C_1-C_4alkyl.

13. A process according to claims 1 and 12, wherein the dye used has the formula (3) or (4) where K_1 is the radical of an amine of the formula (12), (13) or (14) where

R_{15} and R_{16} are each independently of the other hydrogen, methyl, ethyl, methoxy, ethoxy or chlorine, or

R_{15} and R_{17} are together with the nitrogen and carbon atoms joining them together a pyrrolidine, piperidine, morpholine or piperazine ring,

R_{17} and R_{18} are each independently of the other hydrogen, methyl or ethyl, and

R_{19} is hydrogen, methyl or ethyl.

14. A process according to any one of claims 1, 10 and 11, wherein the dye used has the formula (5) where

R_5 is hydrogen or methyl and R_6 and R_7 are each independently of the other hydrogen, C_1-C_2alkyl or C_1-C_2alkoxy, or

R_5 and R_6 are together with the nitrogen and carbon atoms joining them together a pyrrolidine, piperidine, morpholine or piperazine ring.

15. A process according to claim 1, wherein the dye used has the formula (6) where

R_8, R_9, R_{10} and R_{11} are each independently of the others hydrogen or C_1-C_2alkyl, with the proviso that at least one of these 4 substituents is C_1-C_2alkyl and that not all four substituents are ethyl, and

R_{12} and R_{13} are each independently of the other hydrogen, C_1-C_2alkyl or C_1-C_2alkoxy.

16. A process according to claim 1, wherein the dye used has the formula (1) where

R' is hydrogen, C_1-C_2alkyl, amino, C_1-C_2monoalkylamino or di-C_1-C_2alkylamino.

17. A process for dyeing keratin-containing fibres, which comprises treating the fibres with a mixture of at least two cationic dyes having a delocalized positive charge and a cation weight below 300.

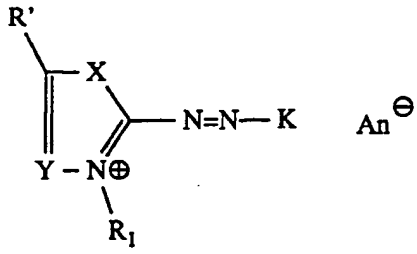
18. A process according to claim 17, wherein the fibres are treated with a mixture of at

least two cationic dyes having a delocalized positive charge and a cation weight below 280.

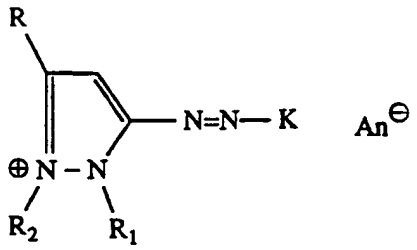
19. A process according to claim 18, wherein the fibres are treated with a mixture of at least three cationic dyes having a delocalized positive charge and a cation weight below 280.

20. A process according to claim 19, wherein the fibres are treated with a mixture of a yellow, a red and a blue cationic dye having a delocalized positive charge and a cation weight below 280.

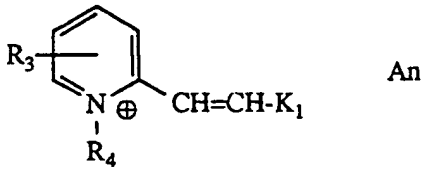
21. A process according to claim 17, wherein the fibres are treated with a mixture of at least two cationic dyes of the formulae



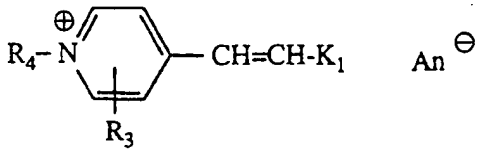
(1),



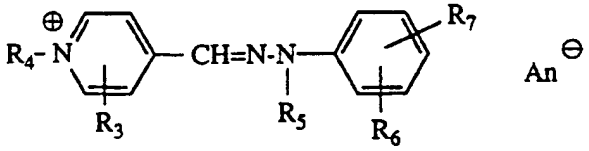
(2),



(3),

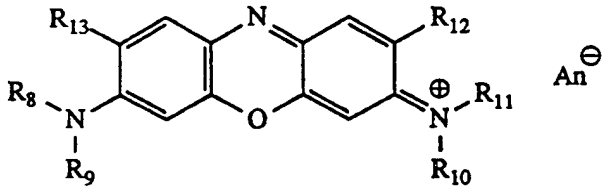


(4),



(5)

or



(6)

where

X is -O-, -S- or $-\underset{\underset{R_2}{|}}{N}-$,

Y is -CH=, $-\overset{\overset{R_2}{|}}{C}=$ or -N=,

R is hydrogen, C_1-C_4alkyl, Cl or nitro,

R' is hydrogen, C_1-C_4alkyl, Cl, nitro, amino, C_1-C_4monoalkylamino or di-C_1-C_4alkylamino,

R_1 and R_2 are each independently of the other unsubstituted or OH-, C_1-C_4alkoxy-, halogen-, CN-, amino-, C_1-C_4monoalkylamino- or di-C_1-C_4alkylamino-substituted C_1-C_4alkyl,

R_3 is hydrogen, C_1-C_4alkyl or CN,

R_4 is unsubstituted or OH- or CN-substituted C_1-C_4alkyl,

R_5 is hydrogen or C_1-C_4alkyl,

R_6 and R_7 are each independently of the other hydrogen, C_1-C_4alkyl or C_1-C_4alkoxy, or

R_5 and R_6 are together with the nitrogen and carbon atoms joining them together a 5- or 6-membered ring,

R_8, R_9, R_{10} and R_{11} are each independently of the others hydrogen or C_1-C_4alkyl,

R_{12} and R_{13} are each independently of the other hydrogen, C_1-C_4alkyl or C_1-C_4alkoxy,
K is the radical of a coupling component of the aniline series or the radical of a heterocyclic coupling component,
K_1 is the radical of an aromatic or heterocyclic amine, and
$An^{\ominus}$ is a colourless anion.

22. A process according to any one of claims 1 to 21 for dyeing human hair.

23. A process according to any one of claims 1 to 21 for dyeing hairs of domestic animals.

24. A process for dyeing hairs of live animals and humans, which comprises using one of the processes of claims 1 to 21 together with colorimetric methods of measurement to obtain predeterminable shades.

25. A cosmetic formulation for hair dyeing comprising at least one of the dyes of the formulae (1) to (6) as set forth in claim 1 and also further assistants.

26. A process for dyeing hairs on live animals and humans, which comprises using a mixture of at least two ready-prepared dyes of the formulae (1) to (6), preferably a mixture of a yellow, a red and a blue dye, together with colorimetric methods of measurement to obtain predeterminable shades.

INTERNATIONAL SEARCH REPORT

Inter. nal Application No
PCT/EP 94/02077

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 A61K7/13

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 A61K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	FR,A,2 140 205 (L'OREAL) 12 January 1973	
A	FR,A,2 099 399 (L'OREAL) 10 March 1972	
A	GB,A,1 211 801 (L'OREAL) 11 November 1970	
A	GB,A,1 249 438 (GILLETTE) 13 October 1971	
A	CHEMICAL ABSTRACTS, vol. 80, no. 24, 17 June 1974, Columbus, Ohio, US; abstract no. 137149, 'Cosmetic preparations containing photosensitive colorants for skin and hair.' page 256 ;column 2 ; see abstract & JP,A,4 877 034 (NIHON)	

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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"P" document published prior to the international filing date but later than the priority date claimed

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
21 October 1994	07. 11. 94

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl, Fax (+ 31-70) 340-3016	Klaver, T

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INTERNATIONAL SEARCH REPORT

Inter. nal Application No
PCT/EP 94/02077

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
FR-A-2140205	12-01-73	BE-A-	784359	04-12-72
		CA-A-	1021324	22-11-77
		CA-A-	1020463	08-11-77
		CH-A-	560539	15-04-75
		DE-A-	2227214	14-12-72
		GB-A-	1360562	17-07-74
		LU-A-	63287	22-01-73
		US-A-	3869454	04-03-75
		US-A-	3985499	12-10-76
		US-A-	4151162	24-04-79
		LU-A-	64565	16-07-73
FR-A-2099399	10-03-72	AT-A,B	306246	15-02-73
		AU-B-	451330	01-08-74
		AU-A-	3186871	01-02-73
		BE-A-	770720	31-01-72
		CA-A-	989403	18-05-76
		CH-A-	540048	28-09-73
		CH-A-	546273	28-02-74
		DE-A,B,C	2138209	03-02-72
		GB-A-	1312745	04-04-73
		LU-A-	61452	10-02-72
		NL-A-	7110541	02-02-72
		SE-B-	366757	06-05-74
		US-A-	3824074	16-07-74
		US-A-	3896117	22-07-75
GB-A-1211801	11-11-70	LU-A-	53050	27-08-68
		DE-A,C	1794404	27-11-75
		DE-A,C	1719377	21-10-71
		FR-A-	1560664	21-03-69
		GB-A-	1211802	11-11-70
		US-A-	3578386	11-05-71
GB-A-1249438	13-10-71	NONE		
JP-A-4877034		NONE		